Theoretical Characterization of deNO$_x$ Catalysis: The Initial Nitrogen Coupling Step

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The microscopic steps involved in the formation of nitrous oxide from two nitric oxides with an Fe(II) catalyst are discussed in the context of an ab initio theoretical study. We find the coupled products energetically accessible given an appropriate ligand backbone (two waters of hydration). Specifically, we find the dinitrogen dioxide cognate 24 kcal/mol below the dinitrosyl reactant FeCl$_2$(NO)$_2$(H$_2$O)$_2$ and the *cis*-hyponitrite isomer only 4 kcal/mol above the dinitrosyl. Further, an orbital correlation diagram is used to assert that the proposed intermediates are kinetically accessible as well. Finally, we utilize the correlation diagram to suggest that the proposed process is kinetically viable for group VI through VIII metal dications.

INTRODUCTION

The catalytic reduction of nitrogen oxides has become increasingly important in recent years due to legislation aimed at reducing emission levels from nonbiological sources (*1*). As nitric oxide is the major NO$_x$ component of exhaust streams (*2*), research has focused on the reduction of nitric oxide. Both homogeneous and heterogeneous deNO$_x$ studies have been performed (*3–6*). The use of base-metal catalysts is of particular interest due to their ready availability and low cost. A transition metal ion of singular importance in pollution control is Fe(II) either as the bulk oxide or ion exchanged into zeolites. These iron systems have been demonstrated to catalyze the conversion of nitric oxide to nitrogen with a coreactant such as CO or H$_2$ (*3, 4*). The mechanism originally proposed by Shelef and Kummer (*7*) consists of a two-stage oxidation reduction sequence. The initial step involves the coupling of two nitric oxides to form nitrous oxide plus an iron oxide.

$$2NO \rightarrow N_2O + \text{‘O’} \qquad (1)$$
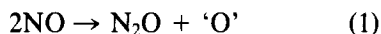
The thus formed nitrous oxide is rapidly re-duced by the catalyst (*3b, 3d, 5*) generating another equivalent of iron oxide.

$$N_2O \rightarrow N_2 + \text{‘O’} \qquad (2)$$
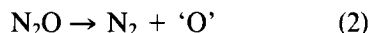
Completing the cycle the two equivalents of iron oxide are reduced by reaction with carbon monoxide forming carbon dioxide plus the regenerated catalytic site.

$$\text{‘O’} + CO \rightarrow CO_2 \qquad (3)$$

Efforts have primarily been directed at characterizing the nitrogen coupling step as this is likely to be the kinetically most difficult step (*3d*). For homogeneous systems this step has been suggested to involve an intramolecular coupling of nitrosyls to form a dinitrogen dioxide ligand (*6a*) which rearranges to a bound *cis*-hyponitrite.

$$\qquad (4)$$
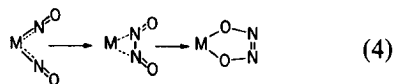
Homogeneous metal hyponitrites have been established to either decompose to nitrous oxide and the metal oxide (*8a*) or react with carbon monoxide to form carbon dioxide and nitrous oxide (*8b–c*).

It should be stressed that transition metal dinitrogen dioxide complexes have never
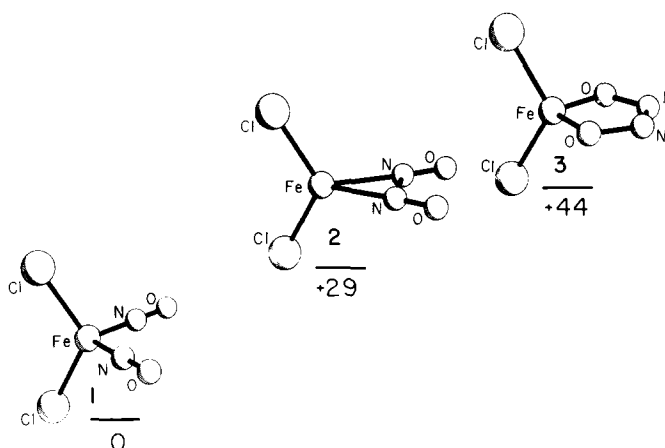
250

FIG. 1. Schematic potential energy profile for the nitrogen–nitrogen coupling step of deNO$_x$ catalysis. The relative energies are in units of kcal/mol. The geometric parameters for **1** are (N–Fe–N)θ = 94.9°, (O–N–Fe)θ = 180°, (Fe–N)R = 1.69 Å, (N–O)R = 1.15 Å; for **2** (N–N–O)θ = 115°, (N–N)R = 1.53 Å, (N–O)R = 1.21 Å, (Fe–N)R = 2.23 Å; for **3** (N–N–O)θ = 118°, (N–O)R = 1.41 Å, (N–N)R = 1.21 Å, (Fe–O)R = 1.74 Å.

been isolated nor unambiguously detected. Further, only a single mononuclear transition metal hyponitrite complex has been identified (*8b*).

Herein we report energetic support for the reaction sequence (4) for a model Fe(II) system: the pseudo-tetrahedral dinitrosyl complex of iron dichloride FeCl$_2$(NO)$_2$ (*9*) and the corresponding dinitrogen dioxide and *cis*-hyponitrite complexes. These coordinatively unsaturated species are not likely to be of direct relevance to homogeneous deNO$_x$ catalysis. However, the structural and energetic insights gained from their study are of qualitative importance to both homogeneous and heterogeneous deNO$_x$ catalysis. The relative energetics and geometries for the chosen dinitrosyl complex **1**, its coupled cognate dinitrogen dioxide complex **2**, and the cis hyponitrite product **3**, are described below and are shown in Fig. 1.

THEORETICAL

The energetics reported in the results section are the differences between GVB-CI (*10a*) calculations for the three species **1, 2,** and **3** (see Fig. 1) or **4, 5,** and **6** (see Fig. 2). The differential effects due to waters of hydration were obtained with a GVB-PP (*10b*) wavefunction (the waters were treated at the Hartree Fock level). The pairs of electrons explicitly correlated were the N–O sigma bonds, the nitrogen s lone pairs, and the ones shown in Fig. 3 (a GVB(12/24) wavefunction). Within this 24 orbital space a R-CI(4) (*10c*) plus R-CI singles times singles CI (*10d*) was performed with a maximum of eight open shell electrons permitted (a total of 11499 spin eigenfunctions and 48921 determinants). Effective potentials were utilized on Fe (*10e*) and Cl (*10f*). The basis set on Cl was a minimum basis set optimized for TiCl$_4$ (*10g*). The s and p basis on Fe was the valence portion of Wachters basis (*10h*) augmented with core functions analogous to those used on Cl (*10f*) (s exponent = 0.4907936, p exponent = 0.1350391). The d basis was the five gaussian basis described previously (*10i*). The N and O basis sets were valence double zeta as discussed previously (*10g*). The basis sets on the waters of hydration were minimum basis sets where the linear parameters were optimized for FeCl$_2$ (H$_2$O)$_2$, the O exponents as above, and the H exponents were Huzinaga's four
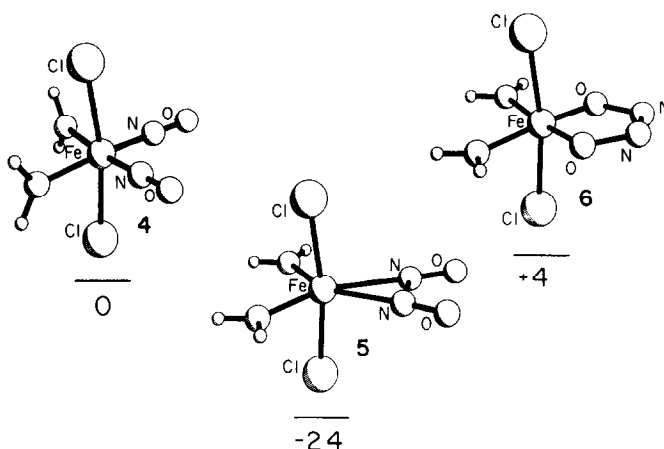
FIG. 2. Schematic potential energy profile for the initial nitrogen–nitrogen coupling step with two waters of hydration present.

gaussian set (*10j*) (scaled by 1.2). Finally the total energies in hartrees for the various species are H_2O (MBS-HF) -75.8858; Complex **1** HF -1198.2835, GVB(12/24) -1198.6370, GVB-CI -1198.7855; Complex **2** HF -1198.3713, GVB(12/24) -1198.6037, GVB-CI -1198.7391; Complex **3** HF -1198.3042, GVB(12/24) -1198.5525, GVB-CI -1198.7161; Complex **4** GVB(12/24) $- 1350.4315$; Complex **5** GVB(12/24) -1350.4822; Complex **6** GVB(12/24) -1350.4101.

For all the molecules the Fe–Cl distance was fixed at 2.30 Å (*11a*). For **1** the Fe–N distance and the N–Fe–N angle were optimized utilizing a GVB-CI (*10c,d*). The N–

FIG. 3. Orbital energy correlation diagram for the initial nitrogen–nitrogen coupling step for $FeCl_2(NO)_2$.

O distance was held fixed at 1.15 Å, a value appropriate for linear nitrosyls (*11d*). For **1, 2,** and **3** the Cl–Fe–Cl angle was fixed at 120.0° (larger than a tetrahedral angle as would be expected for such systems). For complex **2** the Fe–N distance, the N–N distance, and the dependent N–Fe–N angle were optimized with an HF wavefunction. The N–O distance was fixed at 1.21 Å, from the parent nitrosamine (H_2N–NO) (*10d*). The N–N–O angle of 115° was also taken from the parent nitrosamine (*10d*). For complex **3** the Fe–O distance, the N–N distance, and the dependent O–Fe–O angle were optimized with a HF wavefunction. The N–O distance was fixed at 1.41 Å from *cis*-hydroxydiimide (*10d*) (quite close to the 1.39 Å found for the Platinum *cis*-hyponitrite (*8b*)). The N–N–O angle was taken as 118° again from *cis*-hydroxydiimide (*10d*) (also in agreement with the angle from the Platinum *cis*-hyponitrite (*8b*) (118.5°)). For **4, 5,** and **6** nitrogen and oxygen geometries were taken from **1, 2,** and **3,** respectively. The Cl–Fe–Cl angle was increased to 170.0°. Finally, the geometries of the waters of hydration were taken directly from gas phase H_2O, the Fe–O distance of 2.15 was taken from $FeCl_2(H_2O)_2$ (*11e*) and the O–Fe–O angle fixed at 90.0°. For **4** the planes containing the hydrogens and oxy-
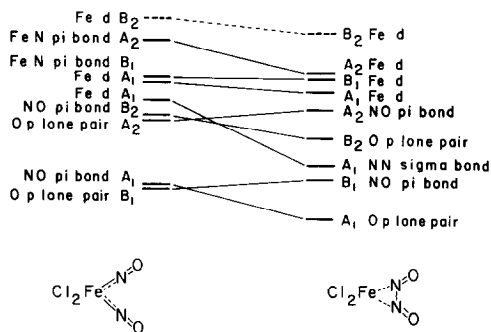
gens of the waters were taken as perpendicular to the plane containing the iron and the two nitrogens. This orientation was found to be more energetically favorable for this complex than the water orientation used for **5** and **6**. For **5** and **6** the water planes were the same as the one containing the iron and the two nitrogens.

RESULTS

The differences in total energies for complexes **1**, **2**, and **3** shown in Fig. 1 suggest that the coupled products **2** and **3** are potentially accessible; **2** is only 29 kcal/mol higher in energy than **1** and **3** only another 19 kcal/mol higher. These species, though unobserved, should be viable given an appropriate ligand backbone. For instance, as shown in Fig. 2, we find waters of hydration to profoundly affect the relative energies of the hydrated forms of **1**, **2**, and **3** (**4**, **5**, and **6**, respectively). Intermediate **5** is 24 kcal/mol more stable than **4** and **6** is only 4 kcal/mol above **4**. This is not surprising as **1** is a 16 electron system, **2** is a 14 electron system, and **3** is a 12 electron system (unusual participation by the pi lone pairs was not observed in the wavefunction of **3** or **6**).

The correlation of high lying orbitals in Fig. 3 demonstrates that the coupling reaction **1** to **2** or **4** to **5** will be thermally allowed (occupied reactant orbitals correlate with occupied product orbitals (*12*)). Further, the LUMO is a nonbonding d orbital of B_2 symmetry indicating that this correlation diagram will be valid for systems with up to 2 more electrons and for paramagnetic Fe(II) systems. Finally, one of the high lying occupied orbitals is a nonbonding A_1 d orbital suggesting that the correlation diagram will be valid for systems with up to two fewer electrons. Thus group VI through group VIII metal dications should have low kinetic barriers for the dinitrosyl coupling step. We propose that the isomerization of **2** to **3** (or **5** to **6**) occurs through a stepwise process. The first step involves a simple rotation of the n^2 nitrogen bound dinitrogen dioxide (**2** or **5**) to an n^5 pi bound dinitrogen dioxide. This intermediate should then readily isomerize to the *cis*-hyponitrite complex (**3** or **6**). Calculations are planned to investigate this hypothesis in detail.

Because Fe(II) dinitrosyls are structurally uncharacterized, because only a single transition metal hyponitrite complex has been structurally characterized, and because dinitrogen dioxide complexes are unprecedented a detailed discussion of the bond distances and bond angles that were optimized is in order. We find the N–Fe–N angle for the dinitrosyl to be 94.9°, as expected for a {M(NO)2}^{8} system (*11d*). The Fe–N distance of 1.69 Å is in agreement with experimental structures for linear iron dinitrosyls (1.66 Å (*13a*) to 1.71 Å (*13b*)). For the dinitrogen dioxide complex **2** we find a N–N distance of 1.53 Å, longer than normal N–N single bonds (ranging from 1.402 to 1.492 Å (*14*)) but still significantly shorter than that for free dinitrogen dioxide (2.24 Å (*15*)). This is consistent with substantial nitrogen–nitrogen sigma bonding. The Fe–N distance found for the dinitrogen dioxide complex (2.23 Å) is in accord with the Fe(II) nitrogen bond distance of 2.26 Å (*16*) in [Fe(C$_4$H$_8$NH)$_6$][Fe$_4$(CO)$_{13}$]. Finally, for the *cis*-hyponitrite complex **3** our Fe–O distance of 1.74 Å compares favorably with 1.69 Å (the sum of the ionic radii for OH$^-$ (1.18 Å) and an estimate for the ionic radius for four coordinate Fe(IV) (0.51 Å) (*17*)). Our N–N distance of 1.21 Å is the same as the N–N distance determined by X-ray crystallography for [(Ph$_3$P)$_2$Pt(N$_2$O$_2$)] (*8b*), the only structurally characterized transition metal complexed *cis*-hyponitrite.

DISCUSSION

We have demonstrated that (4) is a plausible reaction sequence for group VI through group VIII transition metal deNO$_x$ catalysts. Specifically our energetics and correlation diagram suggest that dinitrogen dioxides are thermodynamically and kinetically accessible cognates of dinitrosyl complexes. We believe that these results can be

extended to heterogeneous Fe(II) catalyzed deNO$_x$ processes as well. In fact we speculate that the stretching frequencies observed by Hall (3c) at 1917 and 1815 cm^{-1} are due to bound dinitrogen dioxide which is blue shifted relative to the free compound (which has frequencies at 1870 and 1776 cm^{-1} (18)). This blue shift is possible due to increased NO stretch NO stretch interaction and NO stretch NN stretch coupling brought about by the increased N–N bond order which in turn is caused by the binding to a transition metal ion. Because the coordination sphere of Fe(II) ion exchanged into zeolites is thought to contain at least three oxygen ligands (19) our results suggest the frequencies assigned to a dinitrosyl may instead be due to the kinetically accessible and thermodynamically favored dinitrogen dioxide moiety. Further, it should be noted that dinitrosyl stretching frequencies in homogeneous complexes as high as 1900 cm^{-1} are rare. In conclusion we suggest that the kinetically (and thermodynamically) most difficult step in (4) is the isomerization of the dinitrogen dioxide complex 2 (or 5) to the cis-hyponitrite complex 3 (or 6) and as discussed above our future efforts will focus on determining the barrier for this step and investigate the minimization of it through ligand variation.

ACKNOWLEDGMENTS

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